Interface Reaction and Electrical Contact Properties between Amorphous In-Ga-Zn-O Semiconductor and Cu-MnAlloy Electrode

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論 文 内 容 要 旨

In 2012, oxide semiconductor displays using amorphous In-Ga-Zn-O (a-IGZO) TFTs are starting us in the face for commercial products. A-IGZO TFTs have received great interests because of their high performance TFT characteristics and good reproducibility. These prominent characteristics made a-IGZO a suitable candidate for the channel materials for various display applications such as flexible displays, transparent displays, electric papers and large-sized displays. Among various applications, large-sized and high resolution LCDs will most likely be the first practical application of a-IGZO, since requirements to make displays with high resolution and high frequency are rapidly increasing. The required conditions for these advanced displays cannot be met with conventional processes or pixel architectures using silicon based thin film transistors such as hydrogenated amorphous silicon (a-Si:H) TFTs and low temperature polycrystalline silicon (LTPS) TFTs. In order to replace the silicon based TFTs with the a-IGZO TFTs, we should realize the new optimized considerations, which are a TFT structure, thin film materials and process. Among these considerations, I specially focus on a Cu-based source/drain (S/D) electrode for the a-IGZO TFT. The Cu metallization for the a-IGZO TFT is considered as one of the promising candidate, since it has various advantages such as low cost, low resistance and good productivity. However, it has potential disadvantages such as migration, inter-diffusion and poor adhesion. In this study, I will explore the possibility and the limitation of the Cu-based electrode contacted with the a-IGZO semiconductor for the TFT fabrication. Also, I suggest a Cu-Mn alloy electrode for S/D contact material in order to overcome the problems.

Recently, the Cu-Mn alloy was reported to self-form a diffusion barrier layer on SiOx and glass substrates by the reaction between Mn and the oxide substrate during annealing in a temperature range of 150 to 450 °C. A large solid solubility range of Mn in Cu is also advantageous in producing large-size sputter targets. In the view point of resistivity, the Mn reaction occurred not only at the interface but also on the film surface to form a MnO layer. This leads to a drastic decrease of film resistivity. In particular, a single layer resistivity of Cu-2 at.% Mn alloy became less than 3.0 $\mu\Omega\cdot$cm after annealing at 200–300 °C for 1 h, which is equal to that of Al-based lines. Resistivity could be further decreased to less than 2.0 $\mu\Omega\cdot$cm by using double or triple layers of Cu/Cu-Mn or Cu-Mn/Cu/Cu-Mn under the same annealing condition. The annealing temperature of 200–300 °C for the Cu-Mn alloy is in the same range as the temperature of the final annealing step for the a-IGZO TFT process so as to improve the TFT characteristics. Hence, the annealing process of the Cu-Mn alloy electrode can be implemented to conventional LCD-TFT process without additional process burdens. However, no work has been reported on the Cu-Mn alloy in combination with a-IGZO and its TFT properties in comparison with other low resistance electrodes. In this study, we employed the Cu-Mn alloy as a candidate electrode for the a-IGZO TFT.

In Chapter 4, the IGZO thin films (200nm) were deposited on a glass substrate using RF reactive sputtering. P_{O2} ratios were varied from 0% - 40% O_2 to confirm an amorphous structure of IGZO by X-ray diffraction. IGZO thin films show the stable amorphous phases for various oxygen partial pressures in the as-deposited and the annealed conditions. These a-IGZO thin films have the wide optical band gaps of ~ 3.07 eV and show transparency in the visible region. The increase of the oxygen partial pressure by reactive sputtering leads to gradual changes of the electrical properties from the conductive oxide to the semi-conductive oxide. Diffusion-out Mn from the Cu-Mn thin film by annealing leads to the decrease of film resistivity and the promotion of the good adhesion.

In Chapter 5, Cu-Mn, Ti, Cu and Al electrodes were deposited on a-IGZO. Electrical properties of Cu-Mn alloy electrode were investigated with a special focus on the interface reaction. The Cu and Al electrodes showed non-linear I-V curves, but the Cu-Mn alloy and Ti electrodes showed a linear relation indicating a good ohmic behavior. The specific contact resistance of the Cu-Mn alloy electrodes was in the range of $1.2 \times 10^{-4} \sim 2.9 \times 10^{-4}$ $\Omega \cdot cm^2$. TFT results of Cu-Mn alloy electrode indicated the field effect mobility (μ_{FE}) of 8.21 $cm^2/V \cdot s$, the saturation mobility (μ_{sat}) of 4.80 $cm^2/V \cdot s$, the subthreshold voltage swing (S) of 441 mV/decade and the threshold voltage (V_{th}) of 6.88 V. The TEM, EDS, EELS and SIMS analyses showed the formation of a Mn_xO_y layer accompanying the reduction reaction of a-IGZO to form the layer with In-rich, O-deficient, and containing some Mn. Hall measurement indicated that the reacted a-IGZO layer was the heavily doped n^+ layer with the carrier concentration of 1.40×10^{20} cm^{-3} and the Hall mobility of 12.6 cm^2/Vs. The electron energy band diagram was proposed to show the occurrence of electron tunneling from the Cu-Mn electrode to the highly doped n^+ a-IGZO layer.

In Chapter 6, wet-etching method was employed for a-IGZO TFT with the Cu-Mn alloy electrode, since most Cu-based electrode cannot be clearly etched by dry etching method. For the pattern of S/D electrode on a-IGZO back-channel, the mixed solution of nitric acid (0.25 M) and ammonium persulfate (0.4 M) were used for the high wet-etch selectivity ratio of Cu-Mn / a-IGZO (168.21) and this could control the etching profile of 50°. The a-IGZO TFT with the Cu-Mn alloy electrode by the wet-etching method exhibits μ_{sat} of 6.35 $cm^2/V{\cdot}s$, S of 0.218 V/decade and V_{th} of 3.95 V. Also, the $I_{on/off}$ reached 1.0×10^8 with a low I_{off} of about 10^{-12} A. We employed XPS analysis of the a-IGZO surface in order to evaluate the TFT degradation by etching methods. These results indicated no degradation by wet etchant and small amounts of surface etching can improve TFT performance with the low leakage current. In the contact region, XPS results also suggested that the metal reaction doping increase oxygen vacancies and generate carrier concentration and these also improve TFT performance with the low contact resistance between the Cu-Mn electrode and the a-IGZO channel layer.

Finally, in Chapter 7 we employed TOF-SIMS analysis at the interface between a-IGZO / Cu and Cu-Mn alloy in order to confirm the inter-diffusion of Cu atoms into a-IGZO under long-time thermal stress. MnOx reactants from Cu-Mn alloy electrodes acts as the diffusion barrier of Cu after annealing, while Cu elements from Cu electrodes diffused into a-IGZO. The specific contact resistance with Cu-Mn alloy electrode is dramatically decreased from as-deposited condition to annealed condition, then this somewhat increased as the increase of the thickness of MnOx layer which indicates the tunneling width for free electrons. The source/drain contact resistance under NBTS by the Gated-TML method suggests that the decrease of the contact resistance is not related with MnOx layer but related with the generation of oxygen vacancy under S/D region. Combining the reliability under thermal stress and negative bias, Cu-Mn alloy electrode is very suitable for a-IGZO TFT for future flat panel display applications.

Therefore, these results indicate that the Cu-Mn alloy is a suitable candidate with the low-resistance for the a-IGZO TFT in order to realize next generation displays.

論文審査結果の要旨

本論文は、平面ディスプレイ（FPD）の画素スイッチを構成するIn-Ga-Zn-O薄膜トランジスタ（TFT）とそこに接続するCu-Mn合金配線との界面反応および電気的特性について研究したものである。

近年のFPDにおける大画面化、高精細化、高速度化などの要求を満たすためには、半導体チャンネル層の電子移動度を高めることに加えて、TFTに接続する電極配線の抵抗を減じる必要がある。このため、従来の非晶質シリコン半導体を非晶質In-Ga-Zn-O（IGZO）半導体に転換することによってチャンネル層の高速化を実現する研究が活発である。一方で、配線に求められる条件は、低抵抗であるだけでなく、IGZOと優れた界面密着性を有するとともに、低い界面接触抵抗、熱的に安定な界面構造を有する必要がある。さらに、TFT構造を形成するために、IGZOに対して良好な選択性を有するエッチング工程を開発する必要がある。本研究では、酸化物との密着性と拡散バリア性に優れるCu-Mn合金に着目し、IGZOとの界面に関する特徴を調査するとともに、湿式エッチング法によって作製したTFT特性を評価した。

導電性IGZO上にCu-Mn電極を形成し、250℃で1時間の熱処理を行った。まず、JIS規格に準じたテープテストを行ったところ、全く剥離が生ぜず、優れた界面密着性が得られた。Cu-Mn/IGZO/Cu-Mn間の電流-電圧特性の測定では、良好なオーミック特性が得られ、接触抵抗率は$2x10^{-4}\Omega cm^2$であった。上記の原因を理解するために界面組織の観察ならびに組成分析を行ったところ、MnがIGZOを還元してMnO_x層とInが濃化しOが欠損した変質IGZO層とからなる界面反応層が形成されていることが明らかになった。この変質IGZO層のホール測定を行ったところ、電子濃度が$1.4x10^{20}cm^{-3}$に増加しており、変質層のフェルミ準位が伝導帯最低値より0.08eV高くなっている非縮退状態にあることが判明した。さらに、高温で長時間の熱処理後でも相互拡散は確認できず、MnO_x層が拡散バリア層としての役割も果たしていることが明らかになった。

湿式エッチングは、硫酸ナトリウムと硝酸の混合液が最適であり、適切な混合比にすることでIGZOに対するCu-Mnのエッチング速度を10～20倍速くすることができた。この優れたエッチング選択性を利用してTFTを作製し特性を評価したところ、電界効果移動度が10.2 $cm^2/V.s$、しきい電圧が3.95 V、オン・オフ電流比が10^8など、いずれの項目においても優れた特性が得られた。比較のために、現状の量産材料候補であるTi電極をドライエッチングで形成したTFTも評価した。その結果、電界効果移動度が0.92 $cm^2/V.s$、しきい電圧が5.05 V、オン・オフ電流比が10^5など劣悪な特性であった。XPS分析によれば、両者のTFT特性の差はエッチングによって形成されるダメージの有無および種類に依存することが明らかになった。

得られた結果は、先端FPDのTFTバックプレーンの技術課題を解決するための新材料とプロセス技術を提供するという観点から、産業会から大きい注目を浴びている。さらに、反応によるキャリアドーピングという独創性の高い方法を確立し、金属・酸化物半導体の界面現象において重要な学術的知見を提供した。

よって、本論文は博士(工学)の学位論文として合格と認める。